XXIII. *Experiments on the Formation of Volatile Alkali, and on the Affinities of the Phlogiſticated and light Inflammable Airs. By* William Auſtin, *M. D. Fellow of the College of Phyſicians; communicated by* Charles Blagden, *M. D. Sec. R. S.*

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IN the former part of the year 1787, I undertook to examine the elaſtic fluid produced upon decompoſing volatile alkali by the electric ſtroke, as firſt ſuggeſted by Dr. PRIESTLEY. Some alkaline air being thus decompoſed, and all its inflammable part ſeparated by combuſtion in glaſs veſſels inverted in quickſilver, I obſerved a conſiderable remainder of phlogiſticated air; and after many accurate experiments was fully convinced, that this phlogiſticated air had made a part in the conſtitution of the alkali. This diſcovery induced me to make a variety of ſynthetical experiments on the phlogiſticated and light inflammable airs, with the hopes of forming volatile alkali from its ſimple elements. In this undertaking I alſo derived much aſſiſtance from the ingenious labours of Dr. PRIESTLEY; who, in the courſe of his experiments, had been repeatedly ſtruck with the ſmell of volatile alkali from ſubſtances not ſuppoſed to contain it, and had pointed out ſome important phænomena attending its production. But having acquired a more perfect knowledge of its conſtituent parts, I was enabled to produce volatile alkali in a more ſimple manner, and more demonſtrative of its elements, than he had done.

I was not apprifed, when I had thefe experiments in hand, that the firft object of my inquiry, the decompofition of volatile alkali, and analyfis of its parts, had been fuccefsfully treated by the celebrated M. BERTHOLLET; and that his obfervations had appeared in ROZIER's Journal fome months before. To him therefore I give up that part of the fubject; and fhall confine myfelf in the following obfervations to fome experiments on the formation of volatile alkali, and on the affinities of the phlogifticated and light inflammable airs, which have not, I believe, been hitherto taken notice of.

Firft, I endeavoured to combine the phlogifticated and light inflammable airs, by mixing them together in various proportions in their elaftic ftate, and adding to them fuch fubftances as I thought likely to promote their uniting and forming an alkali. With this view, I threw up to the mixture of thefe airs, marine acid air, the marine and vitriolic acids, to which I alfo joined alkaline air. I tried the effect of cold upon thefe mixtures, by applying to the tubes containing them cloths moiftened with ether. I even paffed the electric fpark repeatedly through them, though with little probability of fuccefs. Laftly, I decompofed alkaline air, and tried to reunite the identical parts which formed it by fimilar additions; but I could not perceive, that in any inftance volatile alkali was produced from its two conftituent parts mixed together in their fimple aëriform ftate.

Yet it is well known, that thefe two bodies unite very readily, when they are not in an elaftic ftate. An unexpected appearance of volatile alkali had been obferved by Dr. PRIESTLEY and Mr. KIRWAN before we were acquainted with its conftitution, and by M. HAUSSMAN fince this difcovery of M. BERTHOLLET. An experiment was exhibited before feveral Gentlemen at Sir JOSEPH BANKS's Houfe, fome years ago,

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in which the quantity of volatile alkali produced is very remarkable. In this experiment a few ounces of powdered tin are moiſtened with ſome moderately ſtrong nitrous acid, and after they have ſtood together a minute or two, about half an ounce of fixed alkali is mixed with them. A very pungent ſmell of volatile alkali is immediately perceived. The experiment ſucceeds equally, if lime be uſed inſtead of fixed alkali. Any perſon, who moiſtens a drachm or two of filings of zinc with a ſolution of cupreous nitre, and, after they begin to act on each other, adds to them a little ſalt of tartar, will find volatile alkali to be produced. Nitrous acid, or cupreous nitre, mixed with iron filings, ſulphur, and a little water, and kept in a cloſe veſſel for ſome hours, yields a ſmell of volatile alkali; and if a piece of paper, ſtained with a vegetable blue ſubſtance, be thrown into the veſſel, it will, in a ſhort time, be turned to a green colour. In each of theſe experiments the nitrous acid and the water are decompoſed. Dephlogiſticated air from each of them combines with the metal, and their other conſtituent parts, the phlogiſticated air of the acid, and inflammable air of the water, being diſengaged at the ſame inſtant, unite and form volatile alkali. Many other ſimilar experiments might be mentioned; but theſe are abundantly ſufficient to prove, that if phlogiſticated and light inflammable air be preſented to each other at the inſtant of their ſeparation from ſolid or liquid ſubſtances, and before their particles have receded from each other, they readily combine and generate volatile alkali.

That theſe two ſubſtances do not combine in their elaſtic ſtate, ſeems to be owing principally to the inflammable air. When theſe two airs combine, it ſeems neceſſary that they part with a certain quantity of that fire to which they owe their elaſticity; and that, unleſs their attraction to each

other exceed their attraction to fire, they will not unite. Even when they are combined in the form of volatile alkali, if heat be applied, they immediately recede from each other, and the alkali is decomposed. When they are not in an aëriform state their attraction to each other is greater, on account of the proximity of their parts; it is then superior to their attraction to fire, and therefore they combine; but when their particles have receded from each other, as in the aëriform state, their attraction to each other is so diminished by the distance of their parts, that their attraction to fire, which is uniform, prevails, and keeps them in a separate state. The specific gravity of inflammable air being eleven times less than that of phlogisticated air, the distance of its particles must be greater than the distance of the particles of phlogisticated air in the proportion of $\sqrt[3]{11}$ to 1, if the elementary particles of the two airs be of equal magnitude; and its effect, on this account, in diminishing attraction must be greater than that of phlogisticated air, in the proportion of, or more probably as the squares of, those numbers.

Whether it be admitted, that fire thus combines with other substances, and is separated from them by their mutual attractions, according to the general law, is not further material to the present enquiry, than as it accounts for a circumstance which seems to be established by the following experiments; namely, that the combination of the phlogisticated and inflammable airs, and the formation of volatile alkali, depends chiefly, if not altogether, on the approximation of the parts of inflammable air, when phlogisticated air is presented to them.

Into a cylindrical glass tube, filled with, and inverted in, quicksilver, I introduced some phlogisticated air, and afterwards some iron filings moistened with distilled water. By this

this arrangement light inflammable air, which is given out from water in contact with iron filings, meeting with phlogiſticated air at the inſtant of its extrication, combines with it, and forms volatile alkali. In order to detect the minute quantities of volatile alkali, which were thus generated, I fixed to the inſide of the glaſs tube a ſmall piece of paper, ſtained with the rind of the blue raddiſh. The vegetable blue was in twenty-four hours changed to a green colour. As an additional proof of the production of volatile alkali, I kept in the ſame tube ſome paper, which had been dipped in a ſolution of cupreous nitre, expecting to ſee its colour converted from green to blue, by the alkali which was to be produced. The green paper became gradually paler, and in a few days the blue colour appeared. This experiment affords a very ſatisfactory demonſtration of the formation of volatile alkali. Water and iron filings mixed together yield inflammable air; but if this be given out in contact with phlogiſticated air, volatile alkali is produced. In theſe circumſtances a double attraction takes place: one part of the water is attracted by the iron; the other is attracted by the phlogiſticated air; and the water ſeems by theſe compound affinities to be much more rapidly decompoſed, than when iron and water are mixed by themſelves.

Volatile alkali is formed in a very few hours, if nitrous air be uſed inſtead of the phlogiſticated, all other circumſtances remaining as in the former experiment. When I have made uſe of nitrous air not well freed from its acid, by which the vegetable blue colour has been turned red, a ſufficient quantity of alkali has been generated in twenty-four hours to change it to a green. If iron filings and water be expoſed to nitrous air for a conſiderable time, the nitrous air is ſo altered that a candle burns in it with increaſed brightneſs, as was obſerved by

Dr.

Dr. PRIESTLEY. This change is accounted for by the formation of the alkali, which depriving the nitrous air of its phlogisticated part leaves a greater proportion of dephlogisticated air.

This experiment also succeeds in atmospheric air, though a longer time is necessary to produce a sensible alteration in the colours employed as tests of the alkali; but the change is very evident in a day or two. Hence we may conclude, that whenever iron rusts in contact with water in the open air, or in the earth, volatile alkali is formed. Phlogisticated air is present in all parts of the terraqueous globe, and operations are constantly going on, by which inflammable air is separated from water, and perhaps from other bodies. Thus we may account for the frequent appearance of volatile alkali in the earth, particularly where inflammable matters abound, among coals and volcanic productions, as also in animal and vegetable substances.

When iron, water, and sulphur act upon each other in atmospheric air, volatile alkali is produced. The eudiometer recommended by SCHEELE is, for this reason, incorrect. Some phlogisticated air disappears, and volatile alkali is formed. This method therefore seems to have misled that great chemist in his analysis of the atmosphere, and induced him to suppose, that the quantity of phlogisticated air in the atmosphere is only $2\frac{2}{3}$ times that of dephlogisticated air.

There is a combination of light inflammable air with sulphur forming hepatic air. It has been observed by the celebrated Mr. KIRWAN, that if nitrous air be mixed with hepatic air volatile alkali will be formed. I have often repeated this experiment, and marked the formation of the volatile alkali by the change of the vegetable blue to a green colour. In hepatic air

air the parts of inflammable air are brought nearer to each other than they are in their ſimple aëriform ſtate *, and therefore the phlogiſticated air of the nitrous air combines with them, and generates volatile alkali.

From all theſe experiments it follows, that whether phlogiſticated air be in a ſtate of purity, or mixed with dephlogiſticated air, as in the atmoſphere, or combined with it as in nitrous air, it will in either caſe unite with the gravitating matter of light inflammable air, provided this ſubſtance be preſented to it in a ſtate of condenſation; but if the circumſtances be reverſed, the ſame combination does not take place. No union is formed between inflammable air and the phlogiſticated part of nitrous air, even though marine acid be added, which, by its attraction to dephlogiſticated air, would contribute to decompoſe the nitrous air, and by its attraction to volatile alkali would tend to unite its conſtituent parts: or if to light inflammable air we add nitrous air and iron filings, no combination enſues; though it has been often obſerved, that volatile alkali is readily generated, when nitrous air is preſented to the inflammable at the inſtant of its extrication from water and iron.

The proportions of the phlogiſticated and inflammable airs in volatile alkali, as diſcovered by calculation, approach very near

* Since theſe experiments were made, I have found that this is not the caſe. The electric ſpark decompoſes hepatic air, and leaves a quantity of inflammable air equal in bulk to the hepatic air very nearly. However, as the inflammable air leaves the ſulphur upon the application of the electrical ſpark, it ſhould ſeem, that the proper matter of inflammable air is more diſpoſed to combine with fire than with ſulphur; which may be the reaſon why hepatic air is decompoſed by nitrous air, while pure inflammable air is not affected by it.

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to the refult of M, BERTHOLLET's experiments. If we take the fpecific gravities of thefe airs, given in Mr. KIRWAN's late publication,

100 cubic inches contain		18,16	grains	of alkaline air.
——	——	—— 30,535	—	of phlogifticated air.
——	——	—— 2,613	—	of inflammable air.

According to M. BERTHOLLET alkaline air is expanded upon decompofitiom from 1,7 to 3,3. Its fpecific gravity after decompofition muft therefore be leffened in the fame proportion; and 100 cubic inches will be found to contain only 9,355 grains of alkaline air thus expanded. In what proportion muft the phlogifticated and inflammable airs be, in order to form a mixture of this fpecific gravity?

Let x reprefent the number of grains of phlogifticated air in 100 cubic inches of the mixture: then $9,355-x$ will exprefs the number of grains of inflammable air. As the weight of one cubic inch is to a cubic inch, fo will the weight of either air in the mixture be to the cubic inches of that air in the mixture; and therefore $\frac{30,535}{100}$ the weight of a cubic inch of phlogifticated air, or which is the fame, ,30535 fhall be to 1, as x is to $\frac{x}{,30535}$ which muft be the number of cubic inches of phlogifticated air in 100 cubic inches of the mixture; and the weight of a cubic inch of inflammable air, that is, $\frac{2,613}{100}$, or $,02613 : 1 :: 9,355-x : \frac{9,355-x}{,02613}$ the cubic inches of inflammable air in 100 cubic inches of the mixture. Thus we have an expreffion for the cubic inches of each air; thefe two quantities taken together are equal to 100 cubic inches by fuppofition. We have then,

$$\frac{x}{,30535} + \frac{9,355 - x}{,02613} = 100;$$

$$x + \frac{2,85654925 - ,30535x}{,02613} = 30,535;$$

$$,02613x + 2,85654925 - ,30535x = ,79787955;$$

$$,27922x = 2,05866970$$

$x = 7,373$ the number of grains of phlogiſticated air in 100 cubic inches, or in 9,355 grains of the mixture; and $9,355 - 7,373 = 1,982$, the grains of inflammable air.

Now 7,373 : 1,982 :: 121 : 32; the quantity of phlogiſticated air is to that of inflammable, as 121 to 32.

According to M. BERTHOLLET's experiments, the quantity of phlogiſticated is to that of inflammable air, as 121 : 29. This is not very wide of calculation. If we conſider the great difficulty of obtaining theſe ſpecific gravities with exactneſs, we muſt be pleaſed to find ſo near a concurrence, and place more confidence in experiments on the ſpecific gravities and combinations of aëriform bodies, than has generally been given them. M. BERTHOLLET's experiments come within $\frac{1}{10}$ of calculation; and this difference will be diminiſhed by two-thirds, if we take the ſpecific gravities of the phlogiſticated and inflammable airs in the proportion of 11 to 1, as he has done, inſtead of Mr. KIRWAN's proportion, which I have followed in this calculation.